Microfaceting and Thermodynamic Stability of the Surface under Chemisorption Conditions

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Abstract—The effect of the adsorption of simple molecules on the excess surface energy of a pure metal surface is evaluated. Even analysis in the framework of simple ideal models of adsorption demonstrates that thermodynamic driving forces resulting from chemisorption can cause surface reconstruction with the formation of microfacets. The validity of this approach for description of real adsorption processes, especially at high adsorbate coverages, is confirmed by the fact that the minimum standard enthalpy of adsorption at which metal surface can lose thermodynamic stability, $(\Delta H^{\circ}_{ads})_{cr}$, is similar to the typical experimental data available on the heat of chemisorption of reactive molecules (CO, H_2, and O_2) on the surface of transition metals (Ag, Pt, Ni, Pd, and Fe).

The microfaceting of a metal surface is well known in catalysis and surface science [1–4]. It is caused by heterogeneous catalytic reactions or by gas chemisorption at sufficiently high pressures. Microfaceting, which is surface reconstruction producing a multitude of regularly arranged nanometer-sized objects, is observed for various metals, including Cu, Ag, Ni, and Pt [2–9]. Depending on the metal, reagent, temperature, and other experimental conditions, facets may have the shape of sloping terraces, round hillocks, or elongated grooves and a size of 1–100 nm. Since this phenomenon is very frequent, we can state that, although each particular microfaceting process is characterized by its own kinetics and texturing properties, the general cause of microfaceting is not related to the structural features or physicochemical properties of the adsorbate or adsorbent. Rather, it comes from thermodynamics.

It is believed that, thermodynamically, microfaceting has much in common with the well-known self-dispersion of matter in the bulk of a condensed phase that takes place once surface tension (excess surface energy) is decreased below a critical level (see, e.g., [10, 11]). Indeed, spontaneous adsorption on metal surface must reduce the excess energy of this surface and thereby decrease the surface tension. This will provide a driving force for surface reconstruction analogous to the self-dispersion of matter in the bulk. There have been attempts to estimate this excess energy, applying methods of atomistic dynamics to the particular case of RuO_2 [12]. Unfortunately, we are not aware of attempts to estimate surface tension for typical gas chemisorption processes and thereby verify the above hypothesis as to the causes of microfaceting.

The main purpose of this study is to estimate the adsorption-induced change in excess surface energy for simple ideal models of adsorption in order to analyze the thermodynamic stability of a surface subjected to chemisorption. Obviously, this approach can reveal thermodynamic driving forces capable of causing spontaneous surface reconstruction and microfaceting.

EFFECT OF CHEMISORPTION FROM THE GAS PHASE ON SURFACE TENSION

In the case of an ideal surface, the effect of molecular adsorption on surface tension σ can easily be evaluated using the thermodynamic definition of this quantity,

$$G = G_v + \sigma S, \tag{1}$$

where G and G_v are the Gibbs energies of the whole system and its bulk phases and S is the interfacial area [13].

Let us find the total change in the Gibbs energy upon isobaric adsorption, assuming that, before chemisorption, σ was equal to σ_0. To do this, let us describe the adsorption of gas B in terms of the chemical variable ξ, which is the extent to which the adsorbable gas is converted into adsorbate.

In the most general case of a stoichiometric chemical reaction, $\sum_i \nu_i A_i = 0$, where ν_i are stoichiometric coefficients ($\nu_i < 0$ for original reactants and $\nu_i > 0$ for reaction products; $i = 1, 2, 3, \ldots$), the change in Gibbs energy for the whole system on completion of the reaction is given by

$$\Delta G = G_{\text{begin}} - G_{\text{end}} = \sum_i \mu_i(\xi)(n_i + \nu_i\xi) - \sum_i \mu_i n_i$$

$$= \sum_i \{\mu_i(\xi) - \mu_i\}n_i + \xi\left\{\sum_i \nu_i\mu_i(\xi)\right\} \qquad (2)$$

$$\equiv \sum_i \{\mu_i(\xi) - \mu_i\}n_i,$$

since, by definition, the condition of thermodynamic equilibrium is expressed as $\sum_i \nu_i\mu_i(\xi) = 0$. Here, A_i is the ith component of the chemical reaction, n_i is the initial number of moles of the ith component in the system, ξ is the value of the chemical variable at equilibrium, μ_i is the initial chemical potential of the ith component, and $\mu_i(\xi)$ is the chemical potential of the ith component at equilibrium.

The adsorption of substance B can be viewed as a chemical reaction between B and active adsorption sites Z. If these sites are on a surface with total area S and their surface concentration is Γ_Z, then, according to Eq. (2), the change in Gibbs energy due to adsorption will be

$$\Delta G = n_B(\mu_B(\xi) - \mu_B) + S\Gamma_Z(\mu_Z(\xi) - \mu_Z),$$

where n_B and μ_B are the initial number of moles and the chemical potential of the adsorbable gas, respectively, and n_Z and μ_Z are the same quantities for unoccupied adsorption sites.

In the case of isobaric and isothermic adsorption, when the concentration of the adsorptive in the gas phase is invariable,

$$\mu_B(\xi) = \mu_B$$

and, accordingly,

$$\Delta G = S\Gamma_Z(\mu_Z(\xi) - \mu_Z).$$

The chemical potential of unoccupied adsorption sites, μ_Z, is a function of the adsorbate coverage of the surface, θ. This function can easily be found for simple ideal models of adsorption. For an ideal surface with like adsorption sites,

$$\mu_Z(\theta) = \mu_Z^\circ + RT\ln(1 - \theta),$$

where μ_Z° is the chemical potential of adsorption sites on the empty surface (per mole of sites) and θ is the total equilibrium coverage of the surface. This formula follows, e.g., from Langmuir's theory applied to ideal adsorption on equivalent adsorption sites.

Therefore, when adsorption on an ideal surface is complete,

$$\Delta G \approx \Gamma_Z S[(\mu_Z^\circ + RT\ln(1 - \theta) - \mu_Z^\circ)]$$

$$= RTS\Gamma_Z\ln(1 - \theta) = S\frac{RT}{sN_A}\ln(1 - \theta),$$

where s is the surface area per adsorption site and N_A is the Avogadro number.

Hence, the Gibbs energy of the whole system after adsorption on the ideal surface is

$$G = G_v + \left[\sigma_0 + \frac{RT}{sN_A}\ln(1 - \theta)\right]S.$$

Thus, considering the thermodynamic definition of excess surface energy (Eq. (1)), the surface tension of the ideal system after adsorption is

$$\sigma = \sigma_0 + \frac{RT}{sN_A}\ln(1 - \theta) \equiv \sigma_0 + \frac{kT}{s}\ln(1 - \theta), \qquad (3)$$

where k is the Boltzmann constant. It is important that this formula for σ is valid for both monomolecular adsorption and other ideal modes of Langmuir adsorption.

As would be expected, adsorption diminishes the excess surface energy, since $\ln(1 - \theta) < 0$. This decrease may be rather large. In principle, at

$$\sigma_0 = -\frac{kT}{s}\ln(1 - \theta)$$

or, which is the same thing,

$$1 - \theta = \exp\left(-\frac{\sigma_0 s}{kT}\right) \equiv \exp\left(-\frac{\sigma_0 sN_A}{RT}\right),$$

where σ can be zero.

Obviously, $\sigma = 0$ means complete destabilization of the surface through loss of thermodynamic stability. As a consequence, the surface can undergo spontaneous reconstruction or even self-dispersion.

The value of θ at which the ideal surface will lose thermodynamic stability can easily be estimated, since $\sigma_0 = (1–2)$ J/m^2 and $s \sim 10$ Å$^2 = 10^{-19}$ m^2 for most metals (see, e.g., [1] and references therein). Therefore, at 300 K ($RT \approx 2.6 \times 10^3$ J/mol),

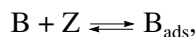$$\frac{\sigma_0 sN_A}{RT} \sim \frac{1\ \text{J/m}^2 \times 10^{-19}\ \text{m}^2 \times 6 \times 10^{23}\ \text{1/mol}}{2.6 \times 10^3\ \text{J/mol}}$$

$$= \frac{1 \times 6 \times 10^4}{2.6 \times 10^3} \approx 20.$$

Thus, $\sigma = 0$ at $1 - \theta \sim \exp(-20)$. This means a very high adsorbate coverage of the surface, for which ideal models of adsorption are obviously invalid. It is nevertheless very interesting to see whether the simplified (ideal) model will predict surface destabilization for, e.g., adsorption of reactive gases on metal surface.

For this purpose, we will consider monomolecular (nondissociative) and bimolecular (dissociative) Langmuir adsorption.

Monomolecular Adsorption

For monomolecular Langmuir adsorption

$$B + Z \rightleftharpoons B_{ads},$$

it is known that

$$\frac{\theta}{P_B(1-\theta)} = K_{ads},$$

where $K_{ads} = \exp(-\Delta G^\circ_{ads}/RT)$ and P_B is the pressure of the adsorptive in the gas phase.

Hence,

$$1 - \theta = \frac{\theta}{P_B K_{ads}}.$$

A large change in excess surface energy is expected at high coverages, when $\theta \approx 1$ and, accordingly,

$$1 - \theta \approx (P_B K_{ads})^{-1}.$$

Therefore,

$$\ln(1-\theta) \approx -\ln P_B + \frac{\Delta G^\circ_{ads}}{RT}$$
$$= -\ln P_B + \frac{\Delta H^\circ_{ads}}{RT} - \frac{\Delta S^\circ_{ads}}{R},$$

where ΔH°_{ads} and ΔS°_{ads} are the temperature-dependent standard enthalpy and entropy of adsorption for substance B.

The surface instability condition is

$$1 - \theta = \exp\left(-\frac{\sigma_0 s N_A}{RT}\right)$$

or

$$\sigma_0 s N_A \approx RT \ln P_B - \Delta G^\circ_{ads} = RT \ln P_B$$
$$- \Delta H^\circ_{ads}(T) + T\Delta S^\circ_{ads}(T).$$

Unfortunately, most publications on the adsorption of reactive gases present measured or calculated values of ΔH°_{ads} but do not report the ΔS°_{ads} values necessary for calculations. Here, we will take a general statistical thermodynamic approach, according to which the decrease in the standard entropy of an adsorptive upon adsorption is equivalent to loss of at least two translational degrees of freedom, so $\Delta S^\circ_{ads} \approx -40$ J mol^{-1} K^{-1}.

This estimate of ΔS°_{ads} and known estimates of σ_0 (see, e.g., [1]) enable one to estimate the minimum critical value of ΔH°_{ads} at which a metal surface can lose thermodynamic stability:

$$-(\Delta H^\circ_{ads})_{cr} \approx \sigma_0 s N_A - T\Delta S^\circ_{ads} - RT\ln P_B. \quad (4)$$

Substitute, into this formula, the following values typical of metals: $\sigma_0 = 1.5$ J/m^2, $s = 10^{-19}$ m^2, and
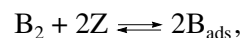
$\Delta S^\circ_{ads} \approx -40$ J mol^{-1} K^{-1}. Assume also that $P_B = 10^{-1}$ bar and $T = 600$ K. This will give

$$(\Delta H^\circ_{ads})_{cr} = 10^{-19} \times 1.5 \times 6 \times 10^{23}$$
$$+ 500 \times 40 - 8.31 \times 500\ln(0.1)$$
$$= (90 \times 10^3 + 20 \times 10^3$$
$$+ 9.6 \times 10^3) \text{ J/mol} \approx 120 \text{ kJ/mol}.$$

This value depends only slightly (logarithmically) on adsorptive pressure and is of the same order as typical values of the heat of nondissociative adsorption of CO on Pt, Pd, Ni, Fe, etc. (120–200 kJ/mol; see, e.g., [14, 15]).

Bimolecular Adsorption

For bimolecular (dissociative) adsorption

$$B_2 + 2Z \rightleftharpoons 2B_{ads},$$

the following relationship is valid:

$$K_{ads} = \frac{\theta^2}{(1-\theta)^2 P_{B_2}}.$$

Therefore, for a high dissociated-adsorbate coverage of the surface,

$$1 - \theta \approx (K_{ads} P_{B_2})^{1/2}.$$

Hence, for critical adsorption, we obtain

$$2\sigma_0 s N_A \approx RT\ln P_{B_2} - \Delta G^\circ_{ads}.$$

Assume, as above, that $\Delta S^\circ_{ads} \approx -40$ J mol^{-1} K^{-1}. The critical heat of adsorption will then appear as

$$-(\Delta H^\circ_{ads})_{cr} \approx 2\sigma_0 s N_A - T\Delta S^\circ_{ads}$$
$$- RT\ln P_{B_2} \approx 210 \text{ kJ/mol}.$$

The values known for the heat of dissociative adsorption, such as H$_2$ adsorption on Pt, Pd, Ni, etc. (100–175 kJ/mol; see, e.g., [14, 16, 17]), fall into the estimated range.

EXPECTED MICROFACET SIZE

Obviously, microfaceting foreshadows complete surface destabilization and occurs before σ falls to zero.

According to Shchukin–Rebinder [11], the maximum particle size r for a thermodynamically stable dispersion in the bulk of a condensed phase is given by the formula

$$\sigma r^2 \sim \beta k T,$$

where σ is the effective surface tension of the dispersed phase and $\beta \sim 15$–30 is a dimensionless quantity depending weakly on the concentration of the dispersed phase and strongly on the particle shape.

Therefore, the typical size of microfacets on a metal surface covered with a large amount of a nondissociated adsorbate can be estimated as

$$r^2 \sim \frac{\beta kT}{\sigma_0 + \frac{kT}{s}\ln(1-\theta)} = \frac{\beta kT}{\sigma_0 - \frac{kT}{s}(\ln P_B + \ln K_{ads})}$$

$$= \frac{\beta kT}{\sigma_0\left\{1 - \frac{kT}{s\sigma_0}\left(\ln P_B - \frac{\Delta G_{ads}^\circ}{RT}\right)\right\}}.$$

For typical metals, $\sigma_0 \sim 1$ J/m^2; hence, at $T \sim 300$–600 K,

$$\frac{\beta kT}{\sigma_0} \sim 10^{-19} \text{ m}^2 = 10 \text{ Å}^2.$$

Therefore, microfaceting yielding facets of size ~10 nm is to be expected at $\sigma \sim 0.01$ J/m^2, when θ is well below its critical level.

For bimolecular adsorption,

$$r^2 \sim \frac{\beta kT}{\sigma_0\left\{1 - \frac{kT}{s\sigma_0}\left(\frac{1}{2}\ln P_{B_2} - \frac{\Delta G_{ads}^\circ}{2RT}\right)\right\}}.$$

Obviously, reconstruction begins before surface destabilization is complete and can show itself only when the heat-treatment time is sufficiently long for rearrangement of the slow atoms of the adsorbent. It can be assumed that the reconstruction of metal surface takes place at the Tammann temperature, at which metals atoms are sufficiently mobile, although this temperature is well below the melting point.

CONCLUSION

The above estimates of the adsorption-induced changes in surface tension are based on ideal models of adsorption on equivalent adsorption sites; therefore, they provide only a rough idea of the real situation. Quantitative description of real chemisorption, particularly at high adsorbate coverages of the surface, will require more detailed models taking into account the interaction of adsorbate molecules and some other factors.

Nevertheless, even the above, very rough estimates indicate that chemisorption from the gas phase onto a metal surface often causes thermodynamic destabilization of the surface, inevitably leading to microfaceting. In terms of the thermodynamic driving force of self-dispersion, microfaceting apparently has much in common with the formation of thermodynamically stable liophilic colloids.

Interestingly, evidence of a large decrease in σ was reported earlier [12], but no conclusions as to surface reconstruction were made.

The new state of surface resulting from microfaceting is of great significance for catalysis. Indeed, for a new state to be stable, surface tension must be positive and rather high. Therefore, either faces characterized by a lower heat of chemisorption must appear on the original surface or new metal–adsorbate structures must result from microfaceting. In the latter case, the heat of chemisorption of new adsorbate molecules must also be lower than is observed for the original surface.

The appearance of new adsorption states characterized by a lower heat of chemisorption as a result of surface reconstrucrtion is well known and is often related to the formation of special, "subsurface" states of the adsorbate [13, 18–20]. For example, for dioxygen chemisorption on silver, which is characterized by an initial heat of chemisorption of $Q_{ads} = 120$–130 kJ/mol [18, 19], chemisorption brings about a new state of adsorbed oxygen, whose heat of chemisorption is $Q_{ads} \sim 100$ kJ/mol [20].

If the assumption as to the origin of this state of oxygen is true, the properties and structure of this state should be discussed in terms of models that are markedly different from conventional models of chemisorption or surface oxide formation.

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